PB-244 404

APPLICATION OF EXCHANGE RESIN FOR TREATMENT OF TEXTILE DYE WASTES

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Bennett College

Prepared for:

National Environmental Research Center

June 1975

DISTRIBUTED BY:

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U. S. DEPARTMENT OF COMMERCE

246076

PB244404

EPA-660/2-75-016
JUNE 1975

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3.
EPA-660/2-75-016		PB 244 404

4. TITLE AND SUBTITLE	5. REPORT DATE
Application of Exchange Resin for Treatment of Textile Dye Wastes	June 1975
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Allison Maggiolo J. Henry Sayles	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Bennett College Greensboro, North Carolina 27420	10. PROGRAM ELEMENT NO. 1BB036
	11. CONTRACT/GRANT NO. R802586
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency National Environmental Research Center-Corvallis Southeast Environmental Research Laboratory College Station Road, Athens, Georgia 30601	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ion Exchange, Cation Exchange, Textile Industry, Wastewater Treatment, Water Reuse, Dyeing, Tertiary Treatment	Textile Industry	05/03

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unlimited	42
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unlimited	$3.75-2.25

EPA Form 2220-1 (9-73)

* U. S. GOVERNMENT PRINTING OFFICE: 1975—698-714/1167 REGION 10

EPA-660/2-75-016
JUNE 1975

APPLICATION OF EXCHANGE RESINS FOR TREATMENT OF TEXTILE DYE WASTES

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Project Number R802586
Program Element 1BB036
ROAP 21 AZT, Task 006

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US ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97330

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

iii

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These results warrant further investigation to determine whether this laboratory success can be translated to commercial utilization.

This report was submitted in fullfillment of Grant Number R802586 by Bennett College, Greensboro, N. C., under the sponsorship of the Environmental Protection Agency. Work was completed July, 1974.

CONTENTS

Sections		Page
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Experimental Phase	5
V	Discussion	10

FIGURES

No.		Page
1	Dye removal column by gravity feed	6
2	Methanol regenerant above column bed	8
3	Mutihead pump drive system with feeds to columns	9
4	Visual comparison of various best runs of color removal for dispersed dyes	31
5	Colorless effluent emerging in flask from XAD-7 over Duolite A-7, runs #40 to 46	32

TABLES

No.		Page
1	Phase 1 - Type of Resin	12
2	Phase 1 - Azo-Dye Removal	13
3	Phase 2 - Removal of Plant Dyes	15
4	Phase 3 - Conditions of Dispersed Dyes	18
5	Phase 3 - Removal of Dispersed Dyes	21
6	Phase 4 - Resin Columns in Tandem with 100% of Mixed Dyes	30

ACKNOWLEDGEMENTS

The authors are indebted to Sy Hall, Arthur Toompas and Tom Alspaugh, Central Research and Engineering, Cone Mills. They provided valuable background information on exchange resin waste treatment and supplied plant dye wastes.

The assistance given by Howard Dixon, Manager of Dyeing, Sellers Manufacturing Dyeing and Finishing, in supplying all the various types of dye waste samples for Phase 2 of this report is greatfully acknowledged.

A major contribution was given by William Simpson, Manager of Dyeing, Glen Raven Hosiery Mills. He not only provided all the dispersed plant dye exhaust samples, but also rendered invaluable technical assistance related to their plant dyeing operation.

Special thanks are due to Thomas N. Sargent, Arthur Burks and Dr. Samuel Karickhoff, personnel, of the Southeast Environmental Research Laboratory for their technical suggestions, literature and arranging for contacts with their professional colleagues working in this field.

Particular appreciation is accorded to Student Assistants Rita Nzeribe, Janice McLean and Nanetta Lowe for their able research assistance. Especially to Miss Lowe are we indebted for her tireless efforts and assistance in obtaining the experimental findings.

SECTION I

CONCLUSIONS

Highly colored azo-dyes were completely removed by basic, neutral and one very weak acid polar resin. However, if the basic resins were in the (OH) hydroxide basic form instead of the (CI) chloride salt form, the dyes were not removed. These same azo-dyes were not removed by weak and strong acid resins.

The main types of actual dye wastes (direct, acid, vat, sulfur, reactive and dispersed) were screened against the various types of resins. The results indicated that all these dyes except dispersed dyes could be removed to give a colorless effluent.

The complete color removal of dispersed dyes was accomplished with a neutral macroreticular resin followed by a weak base resin.

SECTION II

RECOMMENDATIONS

It is recommended that an automatic bench scale pilot unit running continuously from 6 to 15 gal/hr be demonstrated. Probably two (2) different resin columns in series would take care of the majority of types of plant dye waste. As far as practical, the following should be automatic: pumps, adsorption, back washing, elution and regeneration. It should include a semi-continuous solvent stripping unit and continuous spectrophotometer monitor at the column bed discharge to determine when to switch to the regeneration cycle when color of effluent reaches a pre-determined set point. The flow rates, amount of resin and size of equipment should be at a large enough scale to determine the following: (1) the technical success and (2) capital operating costs of a large pilot and full scale plant of the same nature.

At least three different textile mill wastes with three different types of dyes (direct, dispersed and ionic) should be used.

The following three (3) technical goals are recommended:

1. Remove all the types of dispersed dyes as has initially been done with the few used in this study. Until this investigation, little success has been reported in the removal of dispersed dyes by carbon and exchange resin adsorption or activated sludge treatments.

2. Investigate dye wastes that come from dyeing natural fibers (cotton, wool) or their blends to see if they contain enough loose short fibers to clog the resin columns and render them inoperable. If so, see if this can be avoided.

3. Reclaim and re-use the dyes that have been adsorbed from the waste. Where the dyes can't be re-used, blend them as oily solids directly into the plant furnace system as fuel.

SECTION III

INTRODUCTION

BACKGROUND

One of the major problems faced by the textile dyeing industry is the pollution of streams by dyes. This type of water pollution is getting to be a major concern. Highly colored industrial waste streams have been considered to be undesirable, primarily due to their objectionable appearance. Such streams are presently coming under stricter and more specific pollution regulations. A rather high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) accompany the color due to the presence of chemicals in the dye or added as carriers, leveling and wetting agents or buffers to the textile dye bath. Dye waste often contain organically-bound metals such as chromium and copper, that can be toxic to the biological treatment systems as to vegetation and micro-organisms. The same chemistry that gives fabric color-fastness and resistance to bleaching, sunlight, and oxidation makes these dyes similarly resistant to clean-up processes that depend upon degradation as a means of decolorization.

Carbon adsorption has been used. Thermal regeneration of activated carbon is generally accepted as a feasible means of restoring capacity. Thermal regeneration requires transporting the carbon from the decolorization column to a controlled-oxidation furnace, labor to supervise the carefully controlled heating cycle, and finally water quenching the hot carbon before reloading it back into the column. Carbon losses are reported to be 5-10% due to oxidation in the furnace and handling. In addition, where pre-metallized dyes contribute organically-bound metals to the waste stream, thermal regeneration of the activated carbon will often not restore its original efficiency. The organics are burned off, but the metals tend to "enamel" over the adsorption surface, making the carbon less effective after only a few exhaustion cycles. However, polymeric adsorbents can be regenerated with a solvent, eliminating costly thermal regeneration and the problems associated with thermal deposition of metals.

PHASES OF PROJECT

The project was conducted in four phases. The first phase was the preparation of three standard azo-dyes with two, three, and four anionic functional groups. These dyes were then screened against anionic, cationic and neutral polymeric resins. The objective was to determine which would most readily adsorb and remove what type of azo-dyes from their aqueous 1.% solution.

The second phase was to investigate the removal of dyes from actual dye wastes in which azo-dyes are often found. The dye wastes came from direct, acid, dispersed, vat, sulfur, and reactive types of dyeings. These various colored plant dye waste solutions were eluted through glass chromatographic columns containing polymeric adsorbent resins to see which resins would remove the dyes and give a colorless effluent. Also investigated were the regeneration and elution of the adsorbed dyes and the possible continuous re-use of the resins without loss of dye removal efficiency.

The third phase was to investigate the removal of "dispersed dyes" from textile dye waste. Until now, this had not been reported. It is one of the key problems of the textile industries. Most of all classes of possible adsorbent resins were tried.

The fourth phase was optimization and automation.

SECTION IV

EXPERIMENTAL PHASE

PHASE 1 AND 2 - DYE SAMPLE PREPARATION AND EVALUATION

Semi-micro standard pyrex chromatographic 25 ml columns (10 mm I.D. X 250 mm L.) with coarse glass frit discs were used.

All rates of flow for dye-liquors and all columns were held constant at 1 drop per 5 seconds. Gravity feed was used throughout with the same volume of swollen resin (17 ml) and same liquid height over the resin. When necessary in a few cases the rate was held to same 1 drop/5 sec., by adjusting packing density, height of liquor or stop-cock, see Figure 1.

The resin was used in the form supplied as noted in Table 1. Cation resins (acid) were in the H^+ form; anionic resins (basic) were in OH^- or Cl^- form. Most of these commercial resins were 20-50 mesh.

Dye concentration for each of the 3 azo-dye liquors were made as close as possible at 1%.

The total amount of dye liquor used until break through of the color was the amount recorded. This gave a rating of the capacity of each resin. This of course was only part of our objective, the other was the determination of the ease of elution of the dye from these resins and re-use of the resin at acceptable textile mill costs.

PHASE 3 - DISPERSED DYE REMOVAL

The three main areas developed are discussed in this phase.

FLOW RATES

It was convenient in the experiments to measure column flow rates in drops/5 sec in order to control our experiments. Resin column flow rates are usually expressed in bed volumes per hour. There were 10 ± 1 drops in a ml. The rate was 1 drop/5 sec (70 ml/hr) for the 17 ml volume of ion exchange resin. This was equivalent to four bed volumes per hour. Similarly, 2 and 4 drops/5 sec were respectively, eight and sixteen bed volumes per hour. These rates fall within the range of accepted commercial practice for ion exchange usage.

Figure 1. Dye removal column by gravity feed.

COLOR NUMBER

The Perkin-Elmer Double Beam Spectrophotometer #124 was used to determine the 3 highest absorption peaks of Glen Raven Hosiery Mills' dye mix. The dye mix was the four dye formulas mixed in equal amounts. These peaks were 520, 590 and 640 millimicrons. The Spectronic 20 was set at these three wavelengths, and the average of these readings was called the color number. This was an indication of absorption and was based on distilled water being 0.0. However, any turbidity as well as any color gave a higher value. The dye mix waste resulted in complete absorbance a 2.0^{+} number (maximum instrument reading).

REGENERATION

To regenerate 51 ml of Permutit S-2, 50 ml methanol were used to remove the dyes. Initially the methanol containing the dyes was dark and then gradually became colorless as less and less dyes were left on the resin. Then 100 ml of water were used followed by 50 ml of 1.0% HCl. Note the dark color of the methanol regenerate above the column bed, Figure 2. This was repeated for subsequent regenerations. Dowex 4022 (51 ml) used 50 ml of methanol, 75 ml toluene, 50 ml of methanol and 50 ml of water. Almost all of the dye was removed by the 1st 50 ml of alcohol but the resin became white upon using the toluene. Toluene complicated the regeneration process because it is water insoluble. The subsequent aqueous rinses bead up and don't wet the resin unless the remaining toluene is completely removed by a water miscible solvent as methanol above.

PHASE 4 - AUTOMATION AND OPTIMIZATION

This phase was to make the process more continuous and to find the best resin combinations. A multihead pump drive feed system was set up in single and double column tandem operation. This allowed the dye waste to be fed continuously at a constant feed. The usual gravity-manual feed was hard to hold at a constant rate of feed.

The multihead pumps, Figure 3, also permitted us to switch over to the wash and regeneration with methanol cycles without any interruption in time. Two different size glass columns, inside diameter 12 mm and 25 mm, length 600 mm and 400 mm, respectively, were used. The flow rate for dye waste influent, wash and regeneration cycles were 2 ml/min, 0.5 ml/min, and 0.5 ml/min, respectively for the 12 mm ID column packed with 30 ml of resin. Similarly, flow rates for the 25 mm column packed with 70 ml of resin were 4 ml/min, 1 ml/min and 1 ml/min, respectively.

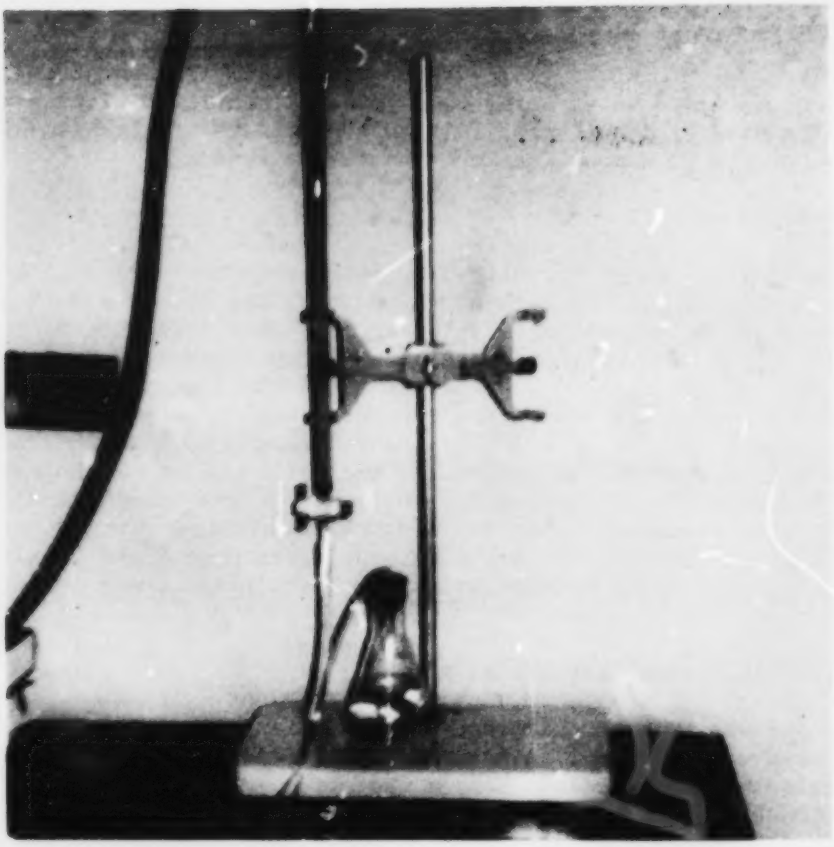


Figure 2. Methanol regenerant above column bed.

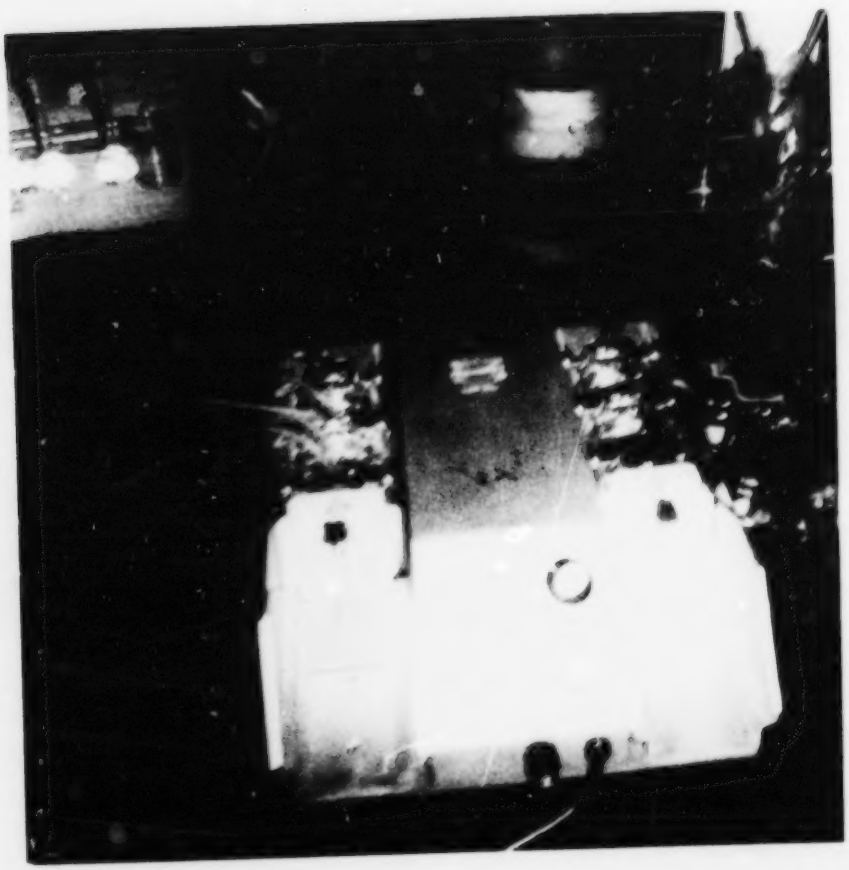


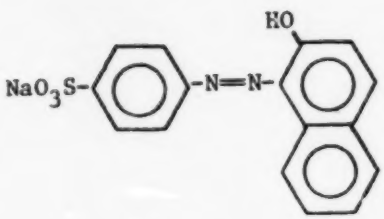
Figure 3. Multihead pump drive system with feeds to column.

SECTION V

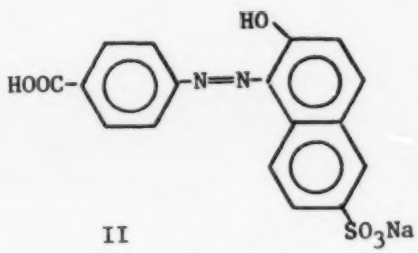
DISCUSSION

PHASE 1

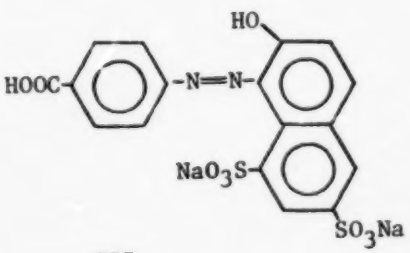
Three (3) azo-dyes were synthesized with an increasing number of acid functional groups and screened against fifteen (15) ionic and neutral polymeric resins. The formulas of the three dyes are as follows:



I



II



III

Dye I has only two (2) functional groups, -OH and NaO_3S-. Dye II has three (3) functional groups, -OH, -COOH and NaO_3S-. It is more acidic because the carboxylic acid group has been added. Dye III has four (4) functional groups, -OH, -COOH and two (2) NaO_3S-.

The removal of azo-dyes by passing synthetic dye solutions through the various types of resins until break thru of some of the dye is shown in Table 2. The three synthetic dye solutions were made to 1.0% by weight of each dye. This was about 10 to 20 times the concentrations of these types of dyes that would actually be left in solution after a typical plant dye had been exhausted in dyeing the textile fabric or yarn.

In Tables 1 and 2, it is clearly evident that five out of six different types of basic resins (both strong and weak base types) were efficient in removing all three types of azo-dyes. From 30 to 40 ml of the dye solutions could be passed through the basic resins before there was any break thru of the dyes. However, it was necessary that these basic resins be in the hydrochloric acid salt form. This is the (Cl) form as shown in Table 1. If the resin was changed to its (OH) form by washing it with 2.0% sodium hydroxide solution, it did not remove the azo-dye from solution. The salt form of Duolite A-7 was washed with 2% sodium hydroxide solution and then with distilled water to remove excess base. The (OH) form of Duolite A-7 did not remove the color of the azo-dye solution. This was apparently the reason why in runs 6, 7, and 8 the resins, in the (OH) form, did not remove the azo-dyes.

The failure of the three resins in their (OH) form to remove the azo-dyes can be explained in terms of pH and ionic attraction. The basic polyamine resin in its hydrogen chloride salt, is represented as Polymer-NR_2HCl. The carboxylic or sulfonic acid group of the soluble dye reacts with the polymeric resin (Polymer-NR_2) via ion-exchange as follows:

$$\text{(insoluble)}\quad \text{Polymer-}\overset{+}{N}R_2H\,\overset{-}{Cl} \;+\; \text{Azo-dye-}SO_3^{-}\,Na^{+}\ \text{(soluble)} \longrightarrow$$

$$NaCl \;+\; \text{(insoluble)}\quad \text{Polymer-}\overset{+}{N}R_2H\,{}^{-}O_3S\text{-Azo-dye}$$

If the column pH is low (<5) the "soluble" salt form of the dye can be converted into the "insoluble" acid form prior to ion exchange in the resin. One of the strong base resins, Run #3, Dowex-11, was not very efficient. Since all the other base resins in their salt form were efficient in azo-dye removal, no further time was spent with Dowex-11.

As seen in Runs #9 and 11, Table 1 and 2, the complete removal of the azo-dyes from their solutions by neutral resins and very weak acid resins can be best explained by the mechanism (2) of physical adsorption described below. It has been reported in Dr. David C. Kennedy's paper, "Molecular Polymeric Adsorbents, " Ind. Eng. Chem. Prod. Res. Develop, Vol. 12, No. 1, 56-61, 1973.

MECHANISMS OF DYE REMOVAL

There are two (2) mechanisms of removal of dyes by exchange resins. Mechanism one (1) is the dye being strongly held by the ionic forces of an ionic resin. As shown above the cationic strong basic resin strongly attracts the anionic sulfonate azo-dye.

Table 1. PHASE 1 - TYPE OF RESIN

Run # Type	Resin	Source	Mesh	Form
1 strong base	Permutit S-2	Ionac	16-50	Cl
2 strong base	Permutit S-2	Ionac	16-50	Cl
3 weak base	Dowex-11	Dow	20-50	Cl
4 weak base	Duolite S-37	Nopco	16-50	Cl
5 weak base	Duolite S-37	Nopco	16-50	Cl
6 weak base	Dowex WGR	Dow	20-50	OH
7 weak base	Amberlite XE-275HP	Rohm & Haas	Unavailable	OH
8 weak base	Amberlite IR-48	Rohm & Haas	Unavailable	OH
9 neutral	Amberlite XAD-7	Rohm & Haas	20-50	Not applicable
10 neutral	Dowex 4022	Dow	20-50	Not applicable
11 slight acid	Duolite S-30	Nopco	Unavailable	Unavailable
12 weak acid	Amberlite IRC-50	Rohm & Haas	Unavailable	H^+
13 strong acid	Bio-Rex 40	Bio-Rad	200-400	H^+
14 strong acid	Dowex 50W-X4	Dow	20-40	H^+
15 strong acid	Amberlite IR-120	Rohm & Haas	20-50	H^+

Table 2. PHASE I - AZO-DYE REMOVAL

Run #	ml at break-thru for dyes			Visual observations of color removal
	Dye I	Dye II	Dye III	
1	40	42	43	Good
2	40	41	42	Good
3	4	4	6	Poor
4	30	32	34	Good
5	31	32	34	Good
6	6	8	9	Poor
7	0	0	0	Could not handle, gave voids
8	0	0	0	No
9	35	38	41	Good
10	0	0	0	No
11	36	39	42	Good
12	0	0	0	No
13	0	0	0	No
14	0	0	0	No
15	0	22	29	Dye I-no, Dye II-fair, Dye III-good

This resin-dye complex is split by strong base solution (2-5% NaOH) which is a stronger base than the basic resin. The equation for the desorption of the dye from the resin and solublization in the regenerated effluent would be as follows:

$$\text{(insoluble) Polymer-}\underset{{}^{-}O_3S\text{-Azo-dye}}{\overset{+}{N}}R_2H + NaOH\ \text{(solution)} \longrightarrow \quad (1)$$

$$\text{(soluble) } NaO_3S\text{-Azo-dye} + \text{(insoluble) Polymer-}NR_2$$

Mechanism two (2) is the hydrophobic resin's removal of soluble organic dyes from aqueous solutions via weak Van der Waal's physical forces. For details of this mechanism see Dr. Kennedy's paper mentioned above. For all practical purposes the attraction of the hydrophobic resin is enough to pull the dyes out of their aqueous solution. An example is Amberlite XAD-2 (styrene-divinylbenzene polymer) which is a macroreticular hydrophobic resin that adsorbs sodium anthraquinone sulfonate from its aqueous solution. To regenerate these polymeric non-ionic adsorbents, the dye-molecule-adsorbent force must only be overcome by the solvating power of the organic solvent on the dye molecule. The dye molecules are not strongly bound (as in the case of ionic attraction, mechanism 1) so that solvent regeneration with methanol is feasible. However, the binding forces are strong enough to allow the adsorbent to remove the dyes.

Weakly basic or acid resins may act also by adsorption via mechanism (2) as well as by its ionic mechanism (1). Dr. David C. Kennedy et al, in a Rohm & Haas company publication, reported a two step regeneration process for weak acid or basic resins, A New Adsorption Ion-Exchange Process For Treating Dye Waste Effluents. This two step regeneration works best with soluble ionic dyes, first using the respective acid or base to return the resin to the non-ionized form (H^+ or OH^+), followed by methanol elution. It is postulated that by first rinsing with acid (for the weakly acid resins) or base (for the weakly base resins) the weak ionic force between the dye molecule and the resin is broken. All that holds the dye to the resin is the weak Van der Waals force. Rinsing with methanol solvates the dye molecule and frees it from the resin. However, in our main work which was involved with removal of dispersed dyes, we only had to regenerate the weak base resin, Duolite A-7, with methanol.

PHASE 2

The results as shown in Table 3 were quite encouraging in that all the dyes from ten (10) different types of actual plant dye wastes taken from three different textile mills were removed except the dispersed dye waste (B-C). Sellers Manufacturing Dyeing and Finishing dye wastes were selected because they use a variety of different classes of dyes: Reactive, Direct, Vat, Sulfur and Union-Wool (acid).

Table 3. PHASE 2 - REMOVAL OF PLANT DYES

Dye #	Type	Dye pH	Permutit S-2 break ml	Permutit S-2 final pH	Duolite A-7 break ml	Duolite A-7 final pH	Duolite S-37 break ml	Duolite S-37 final pH	Duolite S-30 break ml	Duolite S-30 final pH
1-B	Reactive	10.3	25[a]	5.7	75	5.7	a		25[a]	5.7
2-B	Reactive	11.1	25[a]	5.7	100	5.6	a		25[a]	5.7
3-B	Direct	6.5	25[a]	6.0	92	5.5	128	5.2	25[a]	5.8
4-B	Vat	12.6	25[a]	6.1	128	9.9	92	7.4	25[a]	9.8
5-B	Sulfur	11.6	25[a]	5.9	a		a		25[a]	5.9
C.M.	Mixed	8.3	250	4.0	175	5.5	150	4.4	275	4.0
B-C	Dispersed	7.4	200[b]	4.8	200[b]	4.8	200[b]	4.5	a	
11-A	Reactive	10.4	300	4.3	178	4.2	250	4.2	350	4.1
7-A	Reactive	11.0	300	4.2	192	5.6	325	5.7	375	3.9
9-A	Union	4.5	a		a		100	5.0	100	5.2

[a]Ran out of dye waste.
[b]Persistent pink color came thru from start, then deeper color at break.

Cone Mills (C.M.) gave us their worst conglomerate which was a mixture of Direct, Indigo, etc. Cotton dyes. Glen Raven Hosiery dyeing waste (B-C) are singularly interesting because only one type of Dispersed dyes are used throughout the nylon hosiery dyeing industry. All nine wastes were the dye baths at the end of the dyeing cycle without any dilution with rinses or waste water. Cone Mills (C.M.) wastes were diluted by their other plant streams. The four resins used to screen these ten wastes were chosen from Phase 1. They were: strong base (Permutit S-2), weak base (Duolite A-7) and (Duolite S-37) and very weak acid, almost neutral (Duolite S-30). From 100 to 300 ml of dye exhaust were retained by 15 ml of the four resins until break-through, according to what resin and dye were used. This means that 7 to 20 bed volumes of dye liquor may be run through any one of the above four resin columns before the column bed would have to be regenerated. In the cases where the breakthrough amount of dye influent is noted as 25 ml, the liquor ran out before the actual breakthrough of any color. This same dye waste used with reactive and direct dye waste did not breakthrough until between 100 to 300 ml were passed. In regeneration, in almost all cases, the combination of 20 to 30 ml of 2% sodium hydroxide solution followed by 20 ml of wash water and then 20 to 30 ml of methanol between 20° to 40°C was sufficient to remove the dyes successfully. In some cases the methanol or the 2% NaOH solution singularly was able to regenerate the dye waste. Namely, methanol, 20 to 30 ml at 40°C removed dye waste, 2-B and B-C from Duolite A-7 and dye waste B-C and C.M. from Permutit S-2. The 2% NaOH solution, 30 ml at 40°C and 50 ml at 20°C, removed C.M. waste from Duolite A-7.

Table 3 shows that 200 ml of Glen Raven's dispersed dye B-C were added until a decided breakthrough of color. However, from the beginning with all three resins there was always a persistent pink color in the effluent.

Cone Mills' (C.M.) dye was retained until 175, 250 and 275 ml passed through A-7, S-2 and S-3 resins, respectively, before breakthrough of color.

PHASE 3

This phase was with the dyeing waste waters of Glen Raven Mills, Altamahaw plant. They have a dispersed nylon hosiery dyeing operation. Assistance from Ciba-Geigy and Glen Raven Mills established the names, C.I. (Color Index Number) and structural formulas of the main three dyes used. They were: Cibocet Yellow 2GC (C.I. #11855), Cibocet Blue BN (C.E.I. #61505) and Terasil Scarlet B (C.I. #11110). They blend these along with others in different proportions to give standard dye formulas which they use to give varying shades of beige, tan, brown, and an off black mascara. Four of their standard dye formula wastes were used, #334, #339, #515 and #541 and as a mix in equal proportions at 100% conc. or its dilution with water to 75% and 50%. Their dyeing

formula is about 2 to 4% of dyes and 6% of an all in one non-ionic compound which acts as a wetting agent, detergent, dispersant, and antistat. These dyes are colored, particulate, very fine suspensions. Our results show the removal of all of the dyes gives a colorless solution. The resin treatments remove all of the color but a faint white turbidity persists. In attempting to use the Perkin Elmer 120 or the Spectronic-20 to put numerical values on the reduction of color, the usual standard technique is to filter any turbidity whose presence would increase the apparent color number. However, these particular dyes can't be filtered without removing the remaining colored dispersed dyes. Though the color numbers were recorded, samples were retained of the original concentrated dye wastes, their serial dilutions and subsequent ion-exchange treatment for evaluation of key successful runs. However, we have in Table 5 described visually the extent of color removal. In Phase 4, the optimization runs of this Phase 3, Figures 4 and 5 show the total removal of color.

SUMMARY

Strong and weak acid and basic resins were used singly and in tandem. The macroreticular neutral resin XFS-4022 was used by itself in Phase 3. As shown in Tables 4 and 5, the order of efficiency of dye removal as single resins was: (1) Dowex XFS-4022, runs #31 through #34; (2) Amberlite IRC-50, weak acid, runs #35 and #36; (3) Amberlite IR-120, strong acid, see runs #2,6,10,11, and 12; (4) Permutit S-1 and S-2, strong base, runs #3,4,7,8, and 9; (5) the least efficient were the weak base resins, runs #29 and 30.

With two resins in tandem the most efficient combination of resins appears to be when a strong base was over a strong acid resin column, Table 4 and 5, run #27.

DISCUSSION

Pretreatment of the resins have to be carried out according to specific instructions from the manufacturer for that particular resin in order for it to perform properly. The resins, being in different form or treated differently, are subject to different volume changes. Dowex 4022 which is pretreated with methanol swells 10% and then stayed constant. IRC-50, IR-120 and Permutit S-1 increases 1/3 on pre-treating with water and then stayed constant. Duolite A-7 does not change with water but increases 10% on regeneration with methanol and then stayed constant. If we diluted the mixed dye waste from 75% to 50% concentration and passed it thru Dowex XFS-4022, the ml at break went from 390 to 450.

Table 4. PHASE 3 - CONDITIONS OF DISPERSED DYES

Run # resin type	Resin #	Resin ml	pH in dye	pH out dye	Drops/ 5 sec	#Dye[a]
1 strong base	IR-4B	17	9.1	9.1	4	334
2 strong acid	IR-120	17	9.0	3.6	4	339
3 strong base	S-2	30	9.0	6.4	4	339
4 strong base	S-2	17	8.3	6.0	4	Mix[b]
5 strong base strong acid	S-2 IR-120	8 of each	8.3	6.2	4	Mix[b]
6 strong acid	IR-120	17	8.3	2.3	4	Mix[b]
7 strong base	S-2	17	9.4	6.2	4	334
8 strong base	S-2	17	9.0	6.4	4	515
9 strong base	S-2	17	9.1	6.8	4	541
10 strong acid	IR-120	17	9.0	3.5	4	339
11 strong acid	IR-120	17	9.1	3.6	4	515
12 strong acid	IR-120	17	9.2	3.5	4	541

[a]Dye waste used at full strength, if less, % stated.
[b]Mix is the four (4) dye numbered wastes combined in equal amounts.

Table 4 (continued). PHASE 3 - CONDITIONS OF DISPERSED DYES

Run # resin type	Resin #	Resin ml	pH in dye	pH out dye	Drops/ 5 sec	# Dye[a]
13 weak base	A-7	17	9.1	No data	4	334
14 weak acid	A-7	17	9.2	No data	4	339
15 weak acid	A-7	17	9.1	No data	4	515
16 weak acid	A-7	17	9.4	No data	4	541
17	S-2 over	17			4	334
strong base	IR-120	17	9.4	3.0	4	
strong acid						
18 same	Same	17	9.0	3.0	4	339
19 same	Same	17	9.1	3.2	4	515
20 same	Same	17	9.1	3.1	4	200
21 same	Same	17	8.3	3.0	4	Mix[b]
21 continued	Same	17	8.3	3.0	4	Mix[b]
22	IR-120	17	8.3	6.2	4	334
strong acid	over	17		2.3	4	
strong base	S-2					
23 same	Same	17	9.1	6.4	4	515
24 same	Same	17	9.0	6.2	4	541
25 same	Same	17	9.0	6.1	4	339

[a]Dye waste used at full strength, if less, % stated.
[b]Mix is the four (4) dye numbered wastes combined in equal amounts.

Table 4 (continued). PHASE 3 - CONDITIONS OF DISPERSED DYES

Run # resin type	Resin #	Resin ml	pH in dye	pH out dye	Drops/ 5 sec	# Dye[a]
26 same	Same	17	9.0	6.0	4	Mix[b]
27 strong base strong acid	S-1 over IR-120	14 14	8.5 4.7	No data 2.3	2 2	Mix[b]
28 strong acid strong base	IR-120 over S-2	14 14	8.5	6.0 4.5	2 2	Mix[b]
29 weak base	A-7	14	8.5	6.5	1	Mix[b] 50%
30 weak base	A-7	14	8.5	6.5	1	Mix[b] 75%
31 neutral	4022	17	9.0	9.0	1	541 75%
32 same	Same	17	8.5	8.5	1	Mix[b] 75%
33 same	Same	17	8.3	8.3	1	Mix[b] 50%
34 same	Same	51	9.0	9.0	3	541
34 1st regeneration	Same	51	9.0	9.0	3	Same
34 2nd regeneration	Same	51	9.0	9.0	3	Same
34 3rd regeneration	Same	51	9.0	9.0	3	Same
35 weak acid	IRC-50	14	8.0	4.0	1	Mix[b] 75%
36 same	Same	14	8.0	4.0	1	Mix[b] 50%

Table 5. PHASE 3 - REMOVAL OF DISPERSED DYES

Run #	ml at break	Remarks on color	Color number[a]
1	50	Color not removed.	
2	100	Faint pink then much darker at break.	
3	100	Faint blue then much darker at break.	
4	200	Faint tan then column clogged.	1.039
5	400	Faint pink then deeper at break.	
6	400	Faint gray then deeper at break.	1.66
7	400	Faint pink then deeper at break.	
8	400	Same.	
9	400	Same.	
10	400	Faint blue then darker at break.	
11	225	Faint gray then darker at break.	
12	100	Faint pink then darker at break.	

[a]Most of readings not recorded up to run #27. Some anomalous readings due to slight cloudiness.

Table 5 (continued). PHASE 3 - REMOVAL OF DISPERSED DYES

Run #	ml at break	Remarks on color	Color number[a]
13	0	Color not removed.	
14	0	Same.	
15	0	Same.	
16	0	Same.	
17	200	These two columns in tandem gave best results to date. Faint color from start.	1.03
18	200	Same.	
19	200	Same.	
20	200	Same.	
21	200	Same.	
21 continued	200	Regenerated 3 times. Column still as good, same faint pink color.	
22	150	Acid resin over did not remove color as well as Run #17.	0.87 0.75
23	150	Same.	
24	150	Same.	
25	150	Same.	

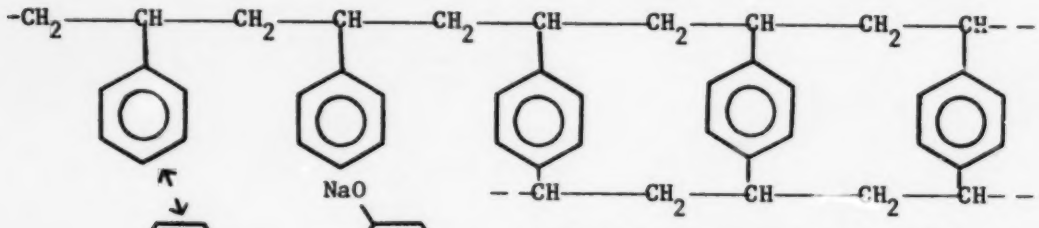
[a]Most of readings not recorded up to Run #27. Some anomalous readings due to slight cloudiness.

Table 5 (continued). PHASE 3 - REMOVAL OF DISPERSED DYES

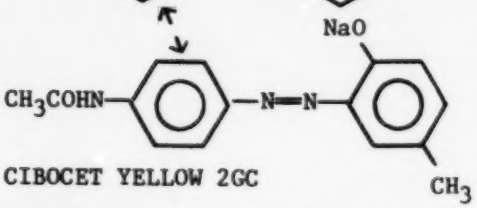
Run #	ml at break	Remarks on color	Color number[a]
26	150	Same.	
27	195	Almost clear pink.	
	195	Same color.	0.112
28	125	Not as efficient as above.	
	125	Pink color.	0.106
29	100	Color came through from start.	2.000+
30	100	Same.	2.000+
31	320	Eluate was clear, then straw color.	1.000
32	390	Same.	0.061
33	450	Clear.	0.006
34	735	Clear and then slight haze, yet no color.	1.01
34 1st regeneration	700	Same.	1.2
34 2nd regeneration	650	Same.	1.2
34 3rd regeneration	600	Same.	1.3
35	100	Same	1.4
36	100	Same	1.2

As discussed under "Mechanisms Of Dye Removal," the chemical equations for the resins' reactions with the dye waste water are below.

In the case of Dowex XFS-4022, the phenomenon involves van der Waal's forces which bind the dye to the solid resin which is a styrene-divinylbenzene copolymer. From a practical concept the hydrophobic or nonpolar aromatic portions of the resin are attracted to the aromatic portions of the dye.



STYRENE DIVINYLBENZENE COPOLYMER

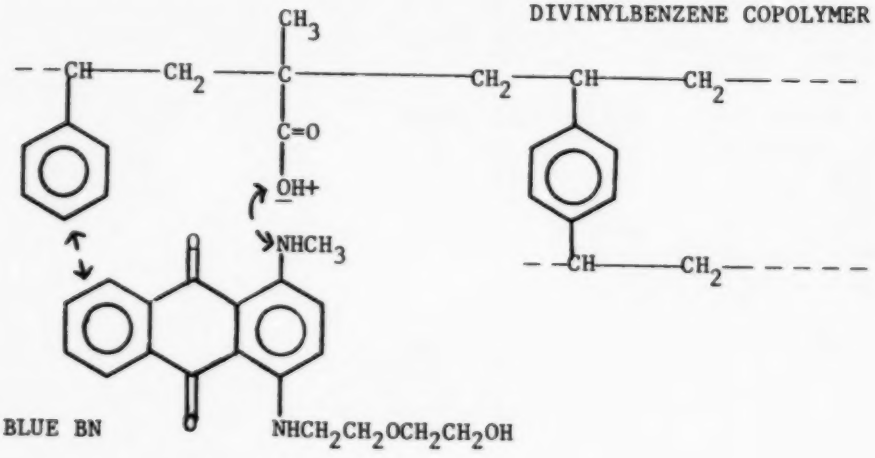


CIBOCET YELLOW 2GC

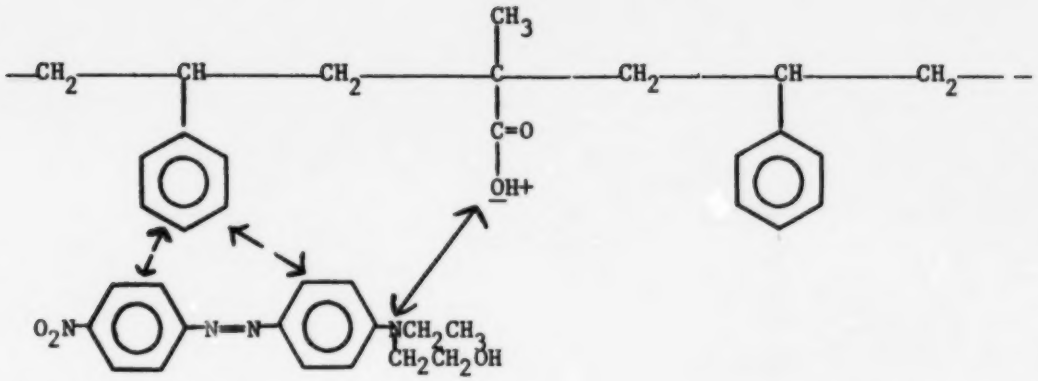
The benzene rings in both the resin and the dye attract each other.

The weak acid resin IRC-50 is a copolymer of methacrylic acid and divinylbenzene. Here not only do the van der Waal's forces work but also the carboxylic acid group of the methacrylic acid copolymer reacts and bonds with the alkyl amino groups in both Cibacet Blue BN and Terasil Scarlet. Also the acid resin reacts with the soluble sodium salt of the Yellow 2GC, which becomes insoluble.

METHACRYLIC ACID-
DIVINYLBENZENE COPOLYMER



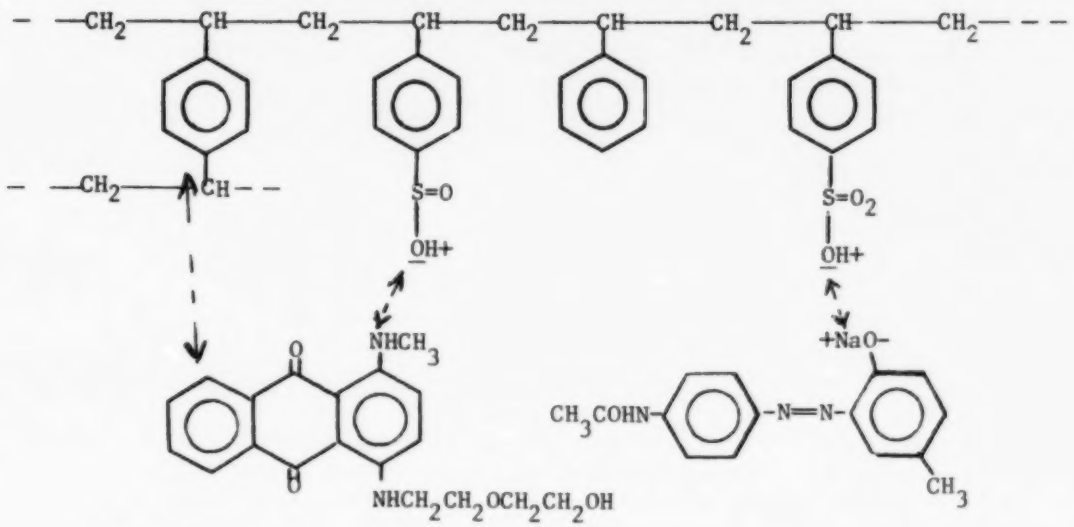
CIBOCET BLUE BN



TERASIL-SCARLET B

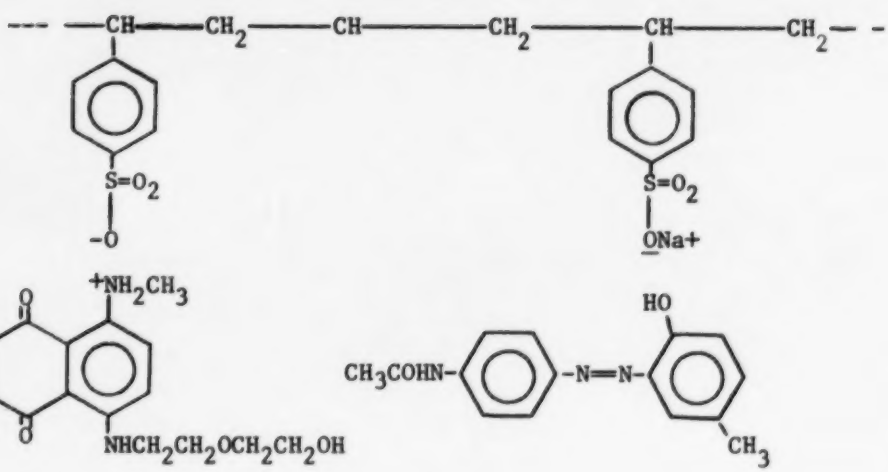
The strong acid IR-120 is a styrene-divinylbenzene sulfonated copolymer. The strong sulfonic acid groups bond to the basic amino groups as the carboxylic acid groups did with the two above dyes. Also it reacts with the sodium salt of Yellow 2GC and precipitates as below.

COPOLYMER OF STYRENE-DIVINYLBENZENE SULFONIC ACID



CIBOCET BLUE BN

CIBOCET YELLOW 2GC

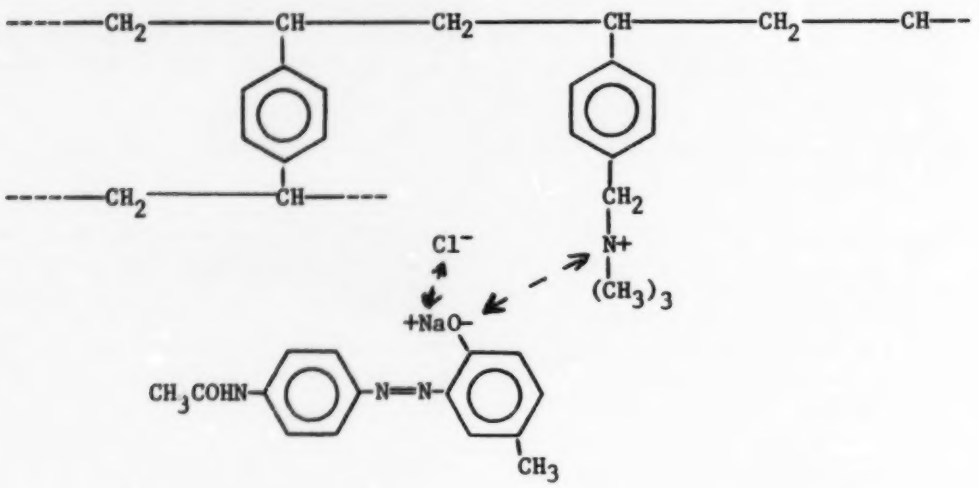


Sulfonic acid of ion-exchange resin forms strong salt bond with basic amino group of Cibocet Blue BN.

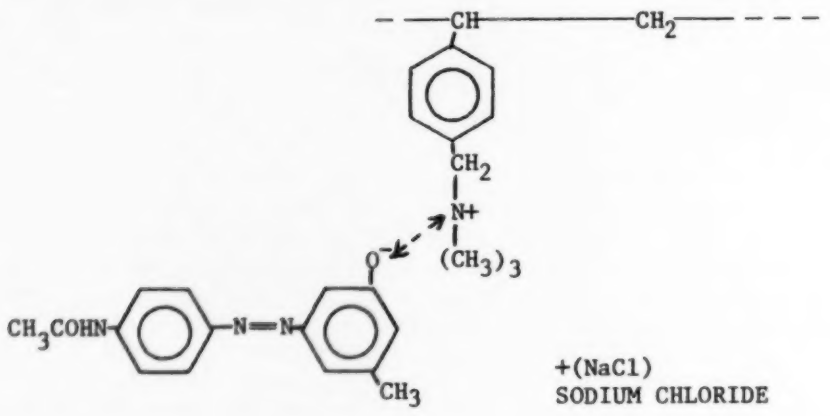
Somewhat soluble salt of Cibocet Yellow 2GC is precipitated as insoluble phenol compound.

The strong basic resins Permutit S-1 and S-2 are styrene-divinyl benzene copolymers with tetraalkyammonium chloride groups. These strong anionic resins having alkylammonium chloride groups will react via ion exchange of Cl^- for dye anions. One can see this when the dye waste which is at a basic pH 8.5 flows down the quarternary ammonium chloride column which is at an acid pH of 4 to 5. Thus, one first observes an acid effluent but the basic pH of the waste keeps neutralizing the acid column until the pH goes up to the 8.5 pH original of the waste. Also the benzene groups, as above, in both the resin and the dye interact via Van der Waal's forces.

PERMUTIT S-1: THE TETRAMETHYLAMMONIUM CHLORIDE COPOLYMER



SALT BONDED COMPOUND OF S-1 WITH CIBOCET YELLOW 2GC



+(NaCl)
SODIUM CHLORIDE

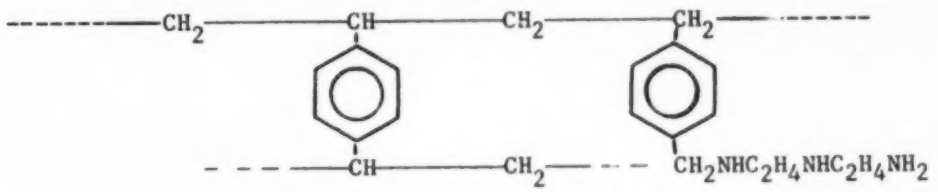
In run #34 the volume of dye removal after three successive regenerations of Dowex-4022 went from 700 ml to 600 ml.

The volume of dye removal for the weak acid resin (IRC-50) is 100 ml, run #35, as compared to 390 ml, run #32, for the neutral resin, Dowex-4022.

We did not notice any physical degradation of the resins in these experiments.

When the dyes and other additives, surfactants, etc. are regenerated with methanol or toluene from neutral resins, they have the same chemical structure as when they were applied.

Most of the structures of the dyes from Glen Raven and all of the resins in the above discussion have been described except Duolite A-7. This is a styrene copolymer with basic amine groups on it as follows:



DUOLITE A-7 STYRENE COPOLYMER

PHASE 4

The ultimate choice of resin and combination of resins is dependent largely on operating costs. The ease of regeneration, maximum number of allowable regenerations (still at same high volume amount of color removal), and the maximum amount of influent before each regeneration are the key cost factors. With these in mind, it was deemed a good choice to use a neutral column as the main column, because the cost and ease of regeneration is much less when you use a cheap neutral organic solvent regenerant. The solvent is easily distilled and reused, but this is not so with aqueous acid and base regenerants. The main reason is that these dispersed dyes are readily soluble in organic solvents such as methanol. They are not soluble (as the mixture of the three chemical dye structures shown in this report) in aqueous caustic solutions, and strong acid solutions only partially dissolve them. Methanol was chosen for these dispersed dyes as the practical regenerant of choice. Neutral solvents also regenerate neutral resins much more efficiently than acid or basic resins. As discussed previously, the neutral resins sorb these dispersed dyes by weak van

der Waal's forces. These dyes are readily removed by the strong solubility effect of the methanol for the dye. However, these same disperse dyes are not soluble in aqueous acid or base solutions that we use and hence do not remove the dyes from either an acid or basic resin.

As seen from Table 6, we selected three sets of resin columns. In all the sets the first column in tandem contained a neutral resin and the second contained either Duolite A-7 (a weak base), Duolite S-30 (a very weak acid), or Amberlite IRC-50 (a weak acid).

The results are shown in Figure 4. Over each test tube is a number as follows: Number (1) the starting dye mix, (2) the effluent just from the XAD-7 resin column, (3) the effluent from the tandem columns of XAD-7 over Duolite A-7 (runs #40 to 46), (4) XAD-7 over IRC-50 (run #37) and (5) XAD-7 over S-30 (run #38). In Figure 5, the deeply colored influent is shown going to the XAD-7 column and then to the Duolite A-7 column where it emerges as a colorless effluent in the receiving flask.

The most efficient combination was the neutral column, XAD-7 followed in tandem with Duolite A-7. All the color was removed by this combination, a very faint colorless turbidity was left which naturally gave some absorption reading on the Spectronic 20. For practical purposes we had removed all the color and left nothing but a trace of opacity. At the suggestion of Dr. Samuel Karickhoff, we investigated this trace of remaining turbidity to see if it was any of the remaining dispersed dyes which now might be colorless being at different pH values. We carefully adjusted this slightly turbid solution in 0.5 pH increments from a pH of 9.0 down to 3.0 and found no color at any pH increment. It does not appear to be any of the original dyes. It may be some oil that was original on the yarn or in the surfactant system.

PRETREATMENT OF RESINS

Thirty milliliters of XAD-7 was transferred to the column by slurry method with distilled water. Then 60 ml water at a rate of 4 bed vol/hr. was passed through. Then 30 ml of methyl alcohol at the same rate followed by a slow water backwash for 10 minutes was added to expand the bed 50%. The bed was then allowed to settle and was ready to accept the influent dye wastes.

Table 6. PHASE 4 - RESIN COLUMNS IN TANDEM WITH 100% OF MIXED DYES

Run #	Resins	ml resin	pH effluent	ml break	Color no.	Remarks
37	XAD-7 over IRC-50	30 over 30	5.1	500	0.88	Not very efficient and difficult to regenerate IRC-50 column.
38	XAD-7 over S-30	30 over 30	6.2	1000	0.47	Duolite S-30 has to be regenerated at the same volume of 1000 ml as XAD-7.
39	4022 over A-7	70 over 70	5.1	500	0.45	The 4022 column has to be regenerated after every 500 ml. Only regenerated this pair two times and stopped.
40	XAD-7 over A-7	30 over 30	5.0	1000	0.43	The best pair of columns by far.
41	Same	Same	6.8	1000	0.44	The XAD-7 column had to be regenerated each time after 1000 ml of dye waste.
42	Same	Same	7.2	1000	0.45	Its bottom column, Duolite A-7, did not have to be regenerated until 5000 ml came from the effluent of its XAD-7 column.
43	Same	Same	8.0	1000	0.44	
44	Same	Same	8.5	1000	0.44	Regenerated Duolite A-7 at Run #46 even though the Color no. is about 0.44.
45	Same	Same	5.0	1000	0.43	All the color has been removed.
46	Same	Same	6.5	1000	0.45	The faint remaining turbidity gave the 0.44 average reading, see photographs.

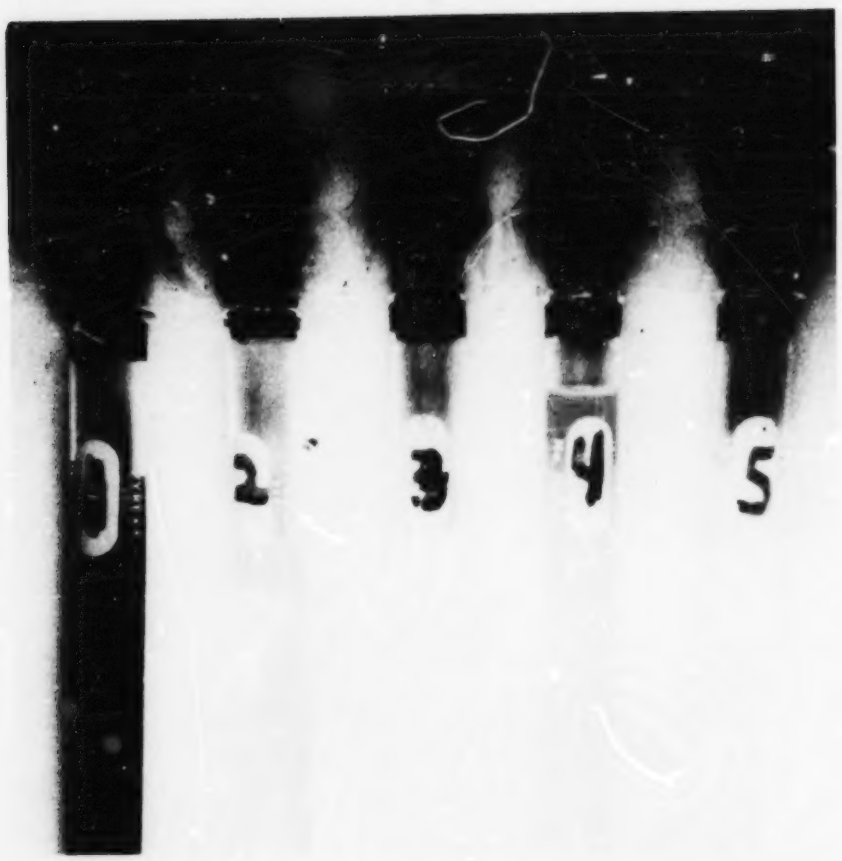


Figure 4. Visual comparison of various best runs of color removal for dispersed dyes.

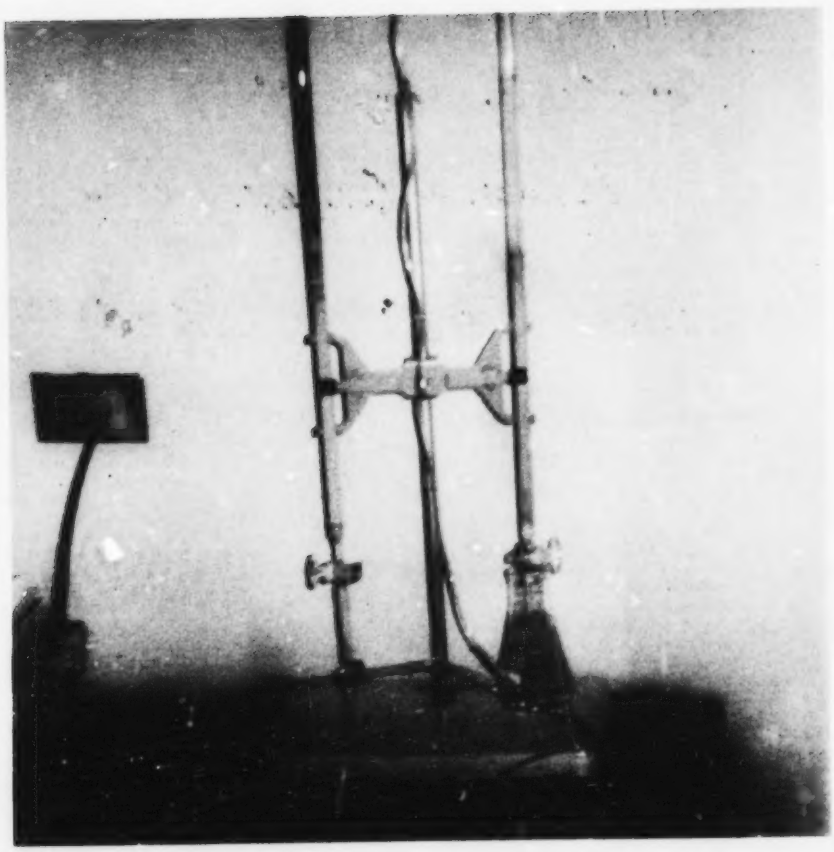


Figure 5. Colorless effluent emerging in flask from XAD-7 over Duolite A-7, runs #40 to 46.

XFS-4022 is transferred dry to the column. Then washed with 2 bed volumes of methanol at 4 bed volumes per hour (4BVH). Finally, it was washed with 2 BV of water at 4BVH and was now ready for use.

Duolite A-7 and S-30 need no pretreatment. They are transferred to column by a slurry of water and are ready to use.

IRC-50 was placed in 3 times its volume of water and stirred with a magnetic stirrer for 3-4 hours and transferred to column for usage.

XAD-7, the most efficient resin, #40, Table 6, was regenerated six times using the following technique at break-point: wash with 50 ml of water at 0.5 ml/min, regenerate with 100 ml methanol at 0.5 ml/min and wash with 50 ml of water. The 100 ml of methanol removed all the dyes from the column. Duolite A-7 which is the 2nd column in tandem had to be regenerated after only 5,000 ml of influent. It was regenerated at 0.5 ml/min with 200 ml of alcohol which removed all the dyes. Then it was put back into its salt form with 60 ml of 1% HCl at 2 ml/min.